

Using A Range of PVB Spinning Solution to Acquire Diverse Morphology for Electrospun Nanofibres

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ABSTRACT: Morphological changes in Polyvinyl Butyral (PVB) electrospun nanofibres can be acquired by preparation of PVB spinning solution in different solvents. Accordingly, three solvents, including ethyl alcohol, n-butanol and isopropanol, with diverse physical properties (e.g. boiling point, density, dipole moment and dielectric constant) were used to prepare PolyVinyl Butyral (PVB) spinning solution. The PVB polymer was used in two ranges of molecular weight. Scanning Electron Microscopy (SEM) was employed to determine the morphological aspects. Results demonstrated a very high increase in the nanofibre diameter, with decreasing dipole moment and increasing boiling point and density of solvents. The smallest nanofibre diameter and bead structure was revealed for the PVB solution prepared by n-butanol. With regard to morphological aspects, isopropanol was selected as the most suitable solvent for a range of PVB molecular weights

KEY WORDS: Electrospinning, Polyvinylbutiral, Nanofibre, Isopropanol, Butanol, Ethanol.

INTRODUCTION

It is possible to produce nanofibres from a wide range of polymers. These fibres have an extremely high specific surface area due to their small diameters, and nanofibre mats can be highly porous with excellent pore interconnection. The fibres also have a high surface to weight ratio, good barrier characteristics against microorganisms and fine particles, a high surface energy that indicates good moisture vapour transmission rates, good strength per unit weight, smoothing and covering effects, low energy requirement for production, etc.

These unique characteristics impart nanofibres with many desirable properties for advanced applications.

PolyVinyl Butyral (PVB) is one of the polymers that have been extensively used in many applications, since PVB is a low-cost alternative, showing flexibility, optical clarity and good adhesion to many surfaces. However, in spite of the extensive literature on PVB polymers, only a limited number of studies were found involving electrospun PVB nanofibres [1-6].

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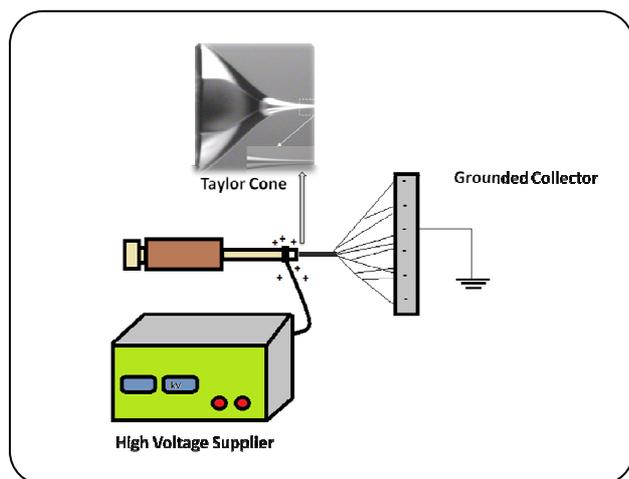


Fig. 1: Diagram of electrospinning set up.

Electrospinning is a technique that involves applying a high voltage between the tip of a syringe and a collector plate, with a polymer solution contained within the syringe and a syringe pump driving the flow of the solution. An electrostatic field is arranged between a nozzle and a collector, and the polymer solution is ejected from the nozzle towards the collector as a result of the electric force shown in Fig. 1 [7-10].

As the intensity of the electric field is increased, the hemispherical surface of the fluid at the tip of the capillary tube elongates to form a conical shape known as a *Taylor cone* [11]. As the repulsive electrostatic force overcomes the surface tension, the charged jet of the fluid is ejected from the tip of the Taylor cone. As the jet moves toward a collector, it elongates, solvent evaporates and fibres are formed on the aluminium foil collector.

The advantage of solution electrospinning is that it can easily form very thin fibres (the average fibre diameter is about 75nm to 500nm), since the viscosity of many polymer solutions is very low. Samples of lower viscosity easily form an elongational deformation. However, the instability of elongational deformation increases with growing deformation of low viscosity polymer solutions. This phenomenon is one of the problems in solution electrospinning, namely, "beads formation". The beads are more easily formed as the fibre diameter decreases. Therefore, it is very difficult to obtain very thin fibre with lower numbers of beads.

There are many parameters that affect the electrospinning process. These can be divided into system and process parameters [12-14]. Viscosity, type of

solvent and polymer, concentration, net charge density (conductivity), surface tension of the polymer fluid and molecular weight can all be identified as system parameters. Applied voltage, flow rate of polymer solution, distance between capillary end and collector, ambient parameters and motion of collector can be identified as process parameters. All parameters have a major role in fibre morphology.

Solvent effect was studied in this work due to the major properties of PVB. It is clear that fibre diameter can be controlled with different solvents. *Kim et al.* investigated the mean diameter of Silk Fibroin (SF), finding it was related to a decrease in formic acid [15]. Different solvents have different properties, such as boiling point, density, dipole moment and dielectric constant. Fibre diameters were found to decrease with increasing density and boiling point of the solvents [16-18].

The spinning of polystyrene was studied in 18 different solvents, and the only solvents found to be used successfully had high values of dipole moment. The results suggested that the important factors determining the electro-spinnability of the as-prepared polystyrene solutions are: high enough values of both the dipole moment of the solvent, and the conductivity of both the solvent and the resulting solutions; a sufficiently high boiling point of the solvent; and lower values of both the viscosity and the surface tension of the resulting solutions [19].

Lubasova et al. explained what are the poor and good solvents for PVB by applying a Hansen Solubility Parameter (HSP). HSP was found to be a useful tool for the prediction of suitable solvents for preparation of the porous nanofibres via the electrospinning process [3]. *Megelski et al.* found trichloromethane or chloroform (CHCl_3) to be the best solvent for producing highly textured Poly(Methyl MethAcrylate) (PMMA) fibres [20].

Few studies have been performed to date on the effect of the dipole moment and dielectric constant on fibre properties [15]. The effects of solvents and their properties on PVB solutions and morphological appearance of the obtained PVB fibres were qualitatively observed by means of a Scanning Electron Microscope (SEM).

EXPERIMENTAL SECTION

Materials and Methods

PVB60H and PVB75H Mowital with 60,000 g/mol and 75,000 g/mol were obtained from Kuraray, Japan.

Table 1: Properties of ethanol, isopropanol and n-butanol solvents.

Solvent	Density (g/ml)	Boiling Point (°C)	Dipole Moment (D)	Dielectric Constant
Ethanol	0.789	79	1.69	24.55
Isopropanol	0.785	82	1.66	18
n-Butanol	0.810	118	1.63	18

Isopropanol, n-butanol of p.a. quality and ethanol were used as solvents. The experimental set-up for electrospinning consisted of a 50-mL syringe and a stainless steel needle positioned horizontally, as shown in Fig. 1.

Solutions of PVB in isopropanol, n-butanol and ethanol with concentrations of 6, 7 and 10 % wt. were prepared.

In electrospinning, a voltage of 30 kV was applied to the solution, and the nanofibres were collected on the aluminium foil collector placed at a distance of 150 mm from the tip of the needle. The flow rate of the polymer solution was 0.5mL/h, the temperature was 21 °C and relative humidity was 45%.

Viscosity (Haake RotoVisco1 at 23 °C) of the polymer solutions was measured. Images of the fibres were taken by SEM (Phenom FEI) and the diameters of the fibres were calculated using the Lucia 32G programme.

Fibre uniformity was calculated using the uniformity coefficient formula, which has the same principle concerning molar mass distribution as in chemistry applications. Fibre uniformity was determined using the number and weight average calculations. The Equations (1) and (2) were used in macromolecular chemistry in order to evaluate numeric and weight average molecular weights [21].

The formulas are as follows:

$$A = \frac{\sum n_i d_i}{\sum n_i} \quad (\text{number average}) \quad (1)$$

$$A_w = \frac{\sum n_i d_i^2}{\sum n_i d_i} \quad (\text{weight average}) \quad (2)$$

d_i = fibre diameter

n_i =fibre number

The fibre uniformity coefficient was determined by ratio A_w/A_n and optimum value, and thus the value should be very close to 1 for uniform fibres. The solvent properties are summarized as Table 1 [22].

RESULTS AND DISCUSSION

Measurement of Viscosity

PVB polymer was dissolved in isopropanol, butanol and ethanol. The viscosity tests were performed as set out in Figs. 2 and 3. Concentration of solution and molecular weight of polymer affect the viscosity, as is known from the literature. The polymer chain entanglements have a significant impact on the breaking up of electrospinning into small droplets or on bead inclusion of electrospun fibres [23]. Although a minimum amount of polymer chain entanglements and, thus, viscosity is necessary for electrospinning, a viscosity that is too high will make it very difficult to pump the solution through the syringe needle [24]. Moreover, according to *Zhong et al.*, when the viscosity is too high the solution may dry at the tip of the needle before electrospinning can be initiated. With increased viscosity, the diameter of the fibre also increases. This is probably due to the greater resistance of the solution to be stretched by the charges on the jet [25, 26].

At low viscosity there is lower chain entanglement between polymer molecules and a higher amount of solvent that leads to beads forming along the fibre.

Figs. 2 and 3 show that different solvents have different viscosity in the same polymer concentrations. Due to their low viscosity, solutions of 6 and 7%wt PVB+n-butanol were not spun. 10% wt PVB+isopropanol solution has a very high viscosity that meant it could not be spun on the electrospinning system.

Ethanol

Ethanol was able to dissolve PVB powder to form a clear solution within one day. Electrospinning was attempted for 6, 7 and 10% wt PVB60H and PVB75H. Viscosity of pure ethanol is around 1.074×10^{-3} Pa.s at 25 °C. PVB polymer solution in ethanol was found to increase from that of the pure solvent. All solutions were easy to spin. However, due to the high viscosity of 10% wt

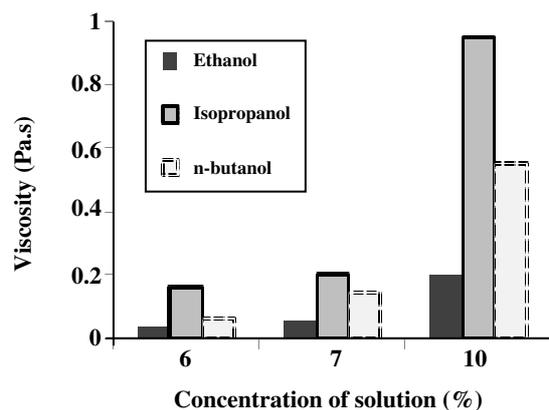


Fig. 2: Viscosity of PVB60H in various concentrations and with different solvents.

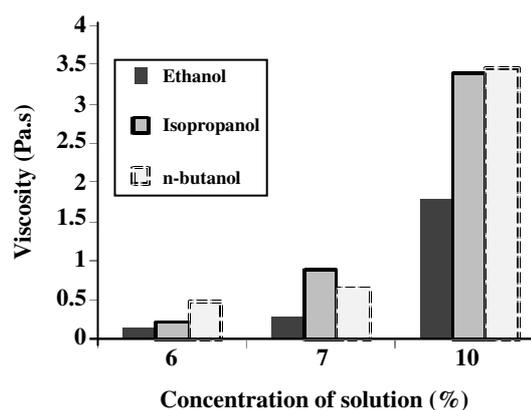


Fig. 3: Viscosity of PVB75H in various concentrations and with different solvents.

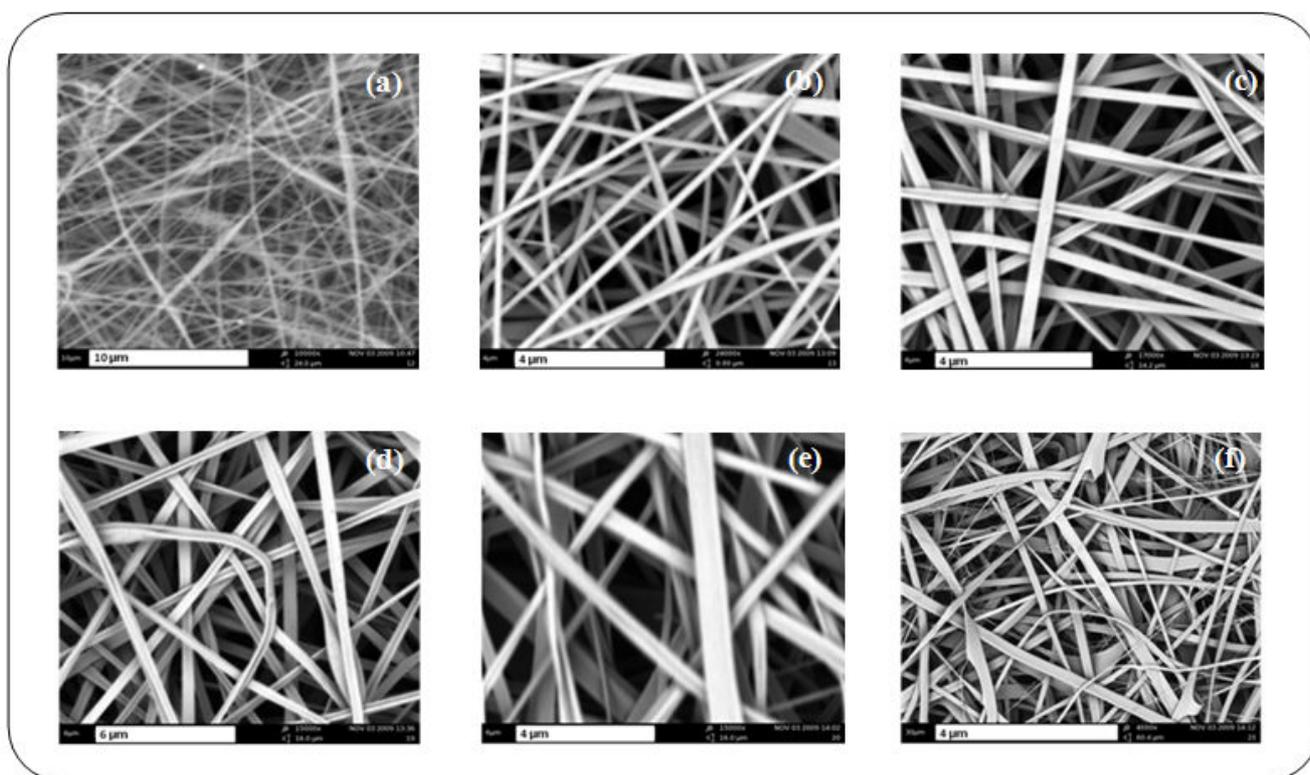


Fig. 4: SEM images of PVB fibre in different concentrations and molecular weight: (a) 6% wt PVB60+ ethanol, (b) 7% wt PVB60+ ethanol, (c) 10% wt PVB60+ ethanol, (d) 6% wt PVB75+ ethanol, (e) 7% wt PVB75+ ethanol, (f) 10% wt PVB75+ ethanol.

polymer solutions, fibre diameters were high. In low viscosity polymer solutions, formation of beads was observed on electrospun nanofibres, such as 6 and 7% wt PVB60H polymer solutions. PVB+ethanol has higher fibre diameter than other solvents. Ethanol has a lower boiling point and higher dipole moment than other solvents (see Table 1). It could therefore be that boiling

point and dipole moment have a large role in nanofibre diameter. SEM images and fibre diameter distribution graphs are shown in Figs. 4 and 5.

Isopropanol

Isopropanol was able to dissolve PVB powder to form a clear solution within one day. Electrospinning was attempted

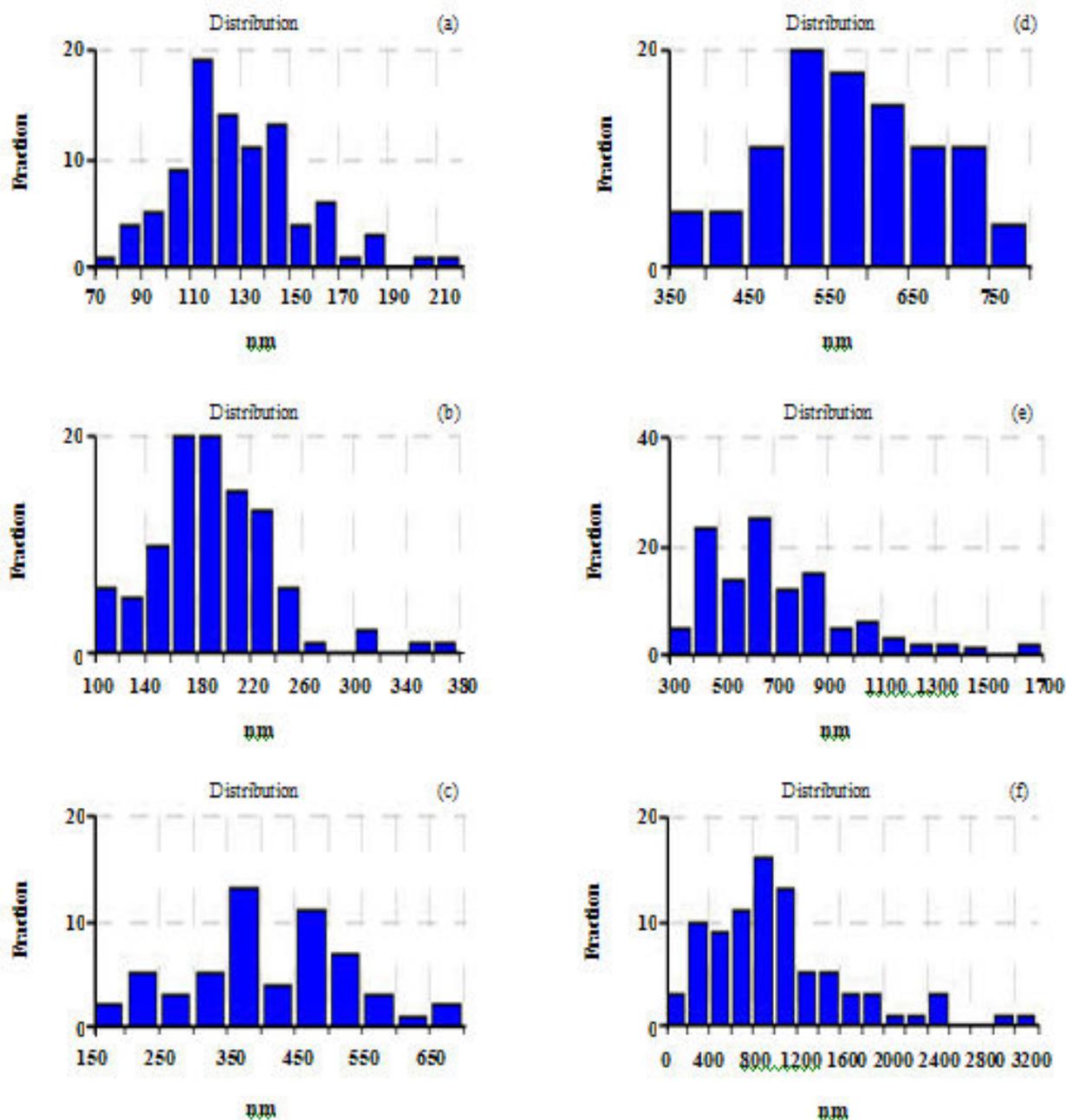


Fig. 5: Fibre diameter and distribution of PVB in ethanol solution: (a) 6% wt PVB60+ ethanol, (b) 7% wt PVB60+ ethanol, (c) 10% wt PVB60+ ethanol, (d) 6% wt PVB75+ ethanol, (e) 7% wt PVB75+ ethanol, (f) 10% wt PVB75+ ethanol.

for 6, 7 and 10% wt PVB60H and PVB75H. The viscosities of 6%, 7%, and 10% wt PVB solutions in isopropanol were found to increase from that of the pure solvent (i.e. 1.96×10^{-3} °C), which was very comparable to the PVB solutions in ethanol, as shown in Figs. 2 and 3. In comparison with ethanol, isopropanol exhibits a higher boiling point and lower dipole moment (See Table 1).

Due to the highly viscous nature of the resulting solutions, only viscosities of 6%, 7%, 10% wt PVB 60H and 6%, 7% wt PVB75H solutions could be spun. Observations under SEM revealed that some smooth and beaded fibres with rough surfaces were occasionally detected. Fibres spun from 6%, 7% wt PVB60H and 6%PVB75H had bead formation on the surface.

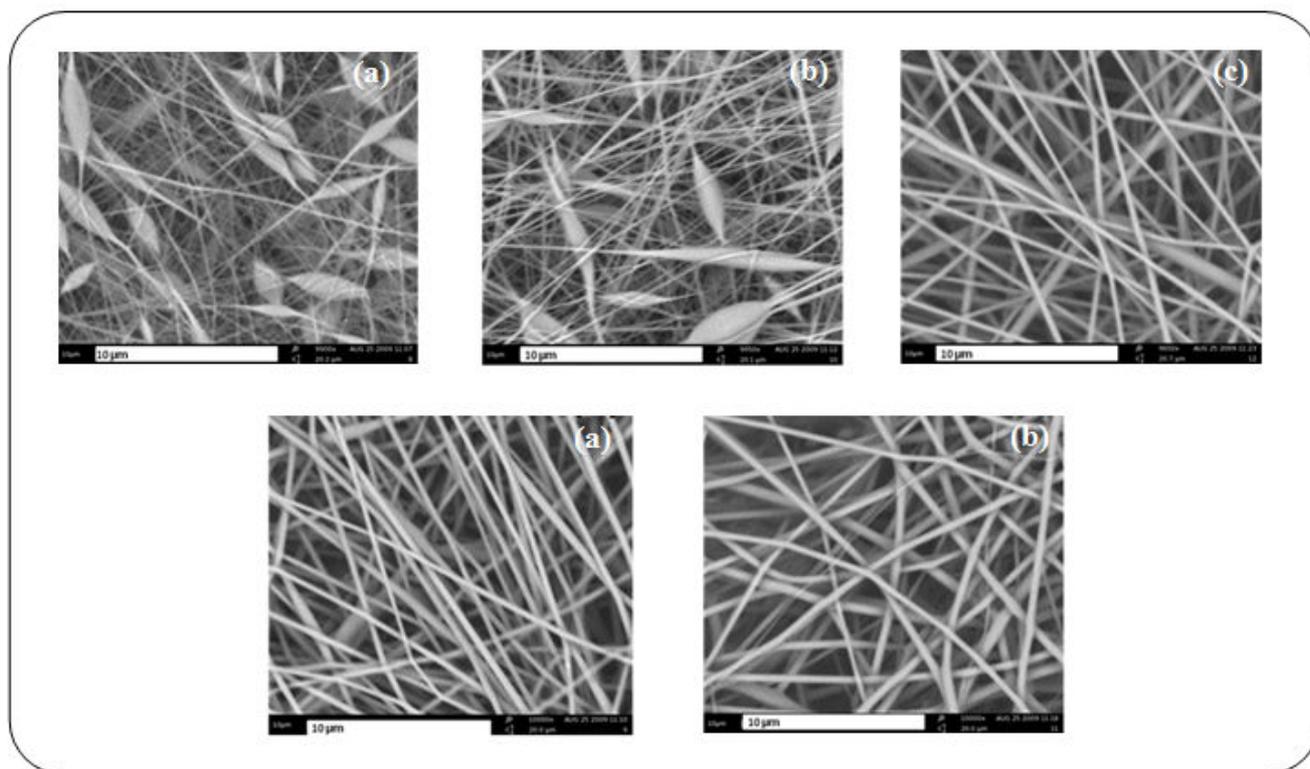


Fig. 6: SEM images of PVB fibre in different concentration and molecular weight: (a) 6% wt PVB60+ isopropanol, (b) 7% wt PVB60+ isopropanol, (c) 10% wt PVB60+ isopropanol, (d) 6% wt PVB75+ isopropanol, (e) 7% wt PVB75+ isopropanol.

SEM images and fibre diameter distribution graphs are shown in Figs. 6 and 7.

***n*-Butanol**

n-Butanol was able to dissolve PVB powder to form a clear solution within one day. Electrospinning was attempted for 6, 7 and 10% wt PVB60H and PVB75H. The viscosities of 6%, 7%, and 10% wt PVB solutions in *n*-butanol were found to increase from that of the pure solvent (i.e. 2.593×10^{-3} °C), which was very comparable to the case for PVB solutions in ethanol and isopropanol, as shown in Figs. 2 and 3. Polymer solutions with butanol had the highest viscosities. In comparison with others, the highest value of the boiling point and density and lowest value of dipole moment was exhibited by *n*-butanol (See Table 1). Interestingly, despite the highest viscosity of PVB+*n*-butanol solution, the finest fibres were spun. Due to the highly viscous nature of the resulting solutions, only the viscosities of 10wt PVB 60H and 6%, 7% wt PVB75H solutions could be spun. Formation of beads was observed on all fibres.

SEM images and fibre diameter distribution graphs are shown in Figs. 8 and 9

In a recent report, six solvents (i.e. acetic acid, acetonitrile, *m*-cresol, toluene, tetrahydrofuran, and dimethylformamide) with different properties (e.g. density, boiling point, solubility parameter, dipole moment, and dielectric constant) were used to prepare electrospun PolyStyrene (PS) fibres. Fibre diameters were found to decrease with increasing density and boiling point of the solvents. A large difference between the solubility parameters of PS and solvent was responsible for the ‘bead-on-string’ morphology observed. Productivity of the fibres (the numbers of fibre webs per unit area per unit time) was found to increase with increasing dielectric constant and dipole moment of the solvents [16].

With regard to the spinning of three types of solvent of PVB at various molecular weights, isopropanol was found to be the best solvent for PVB nanofibres. All solutions were easily spinnable. It seems that dipole moment and boiling point of solvents both affect the fibre

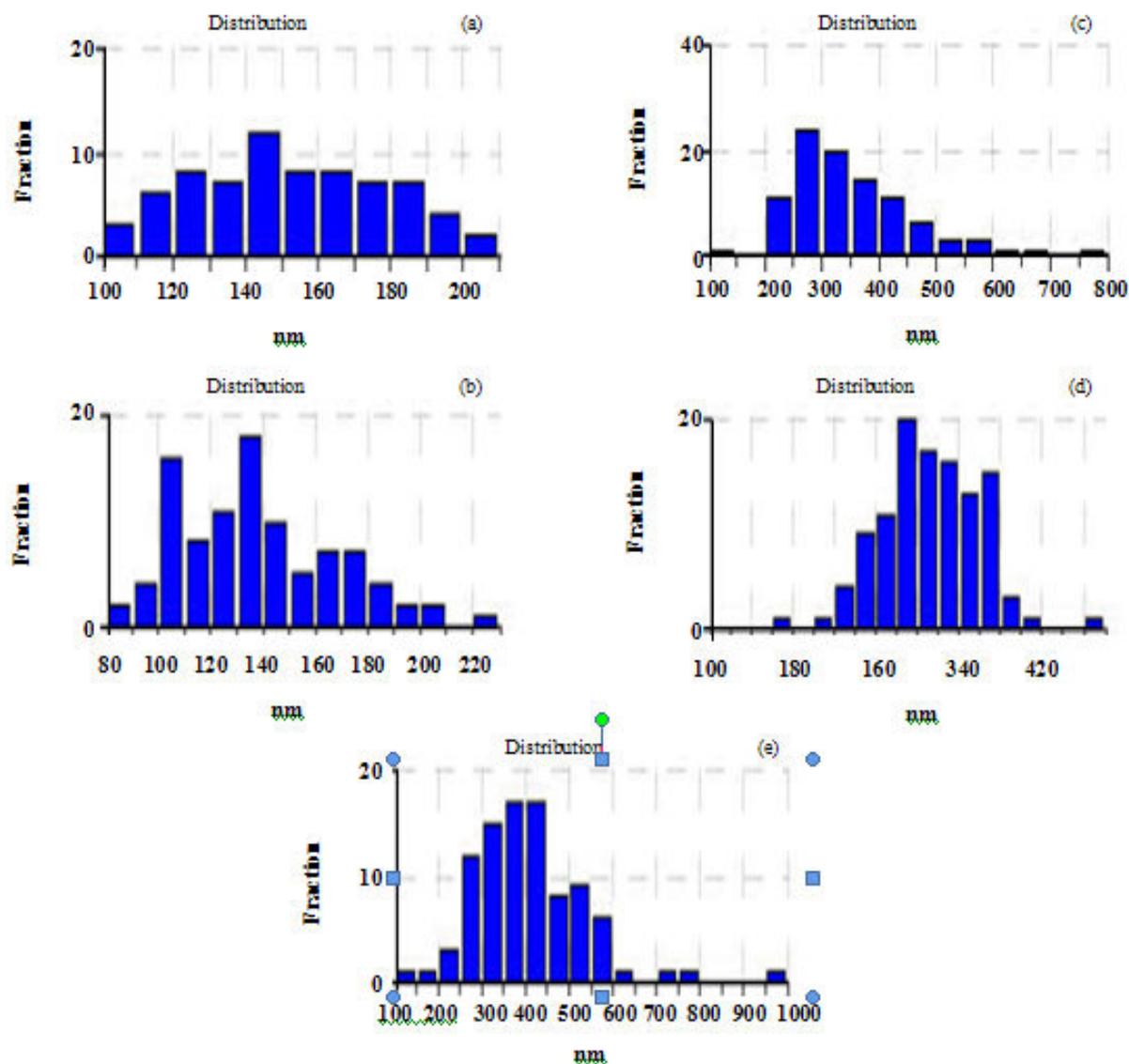


Fig. 7: Fibre diameter and distribution of PVB in isopropanol solution: (a) 6% wt PVB60+ isopropanol, (b) 7% wt PVB60+ isopropanol, (c) 10% wt PVB60+ isopropanol, (d) 6% wt PVB75+ isopropanol, (e) 7% PVB75+ propanol.

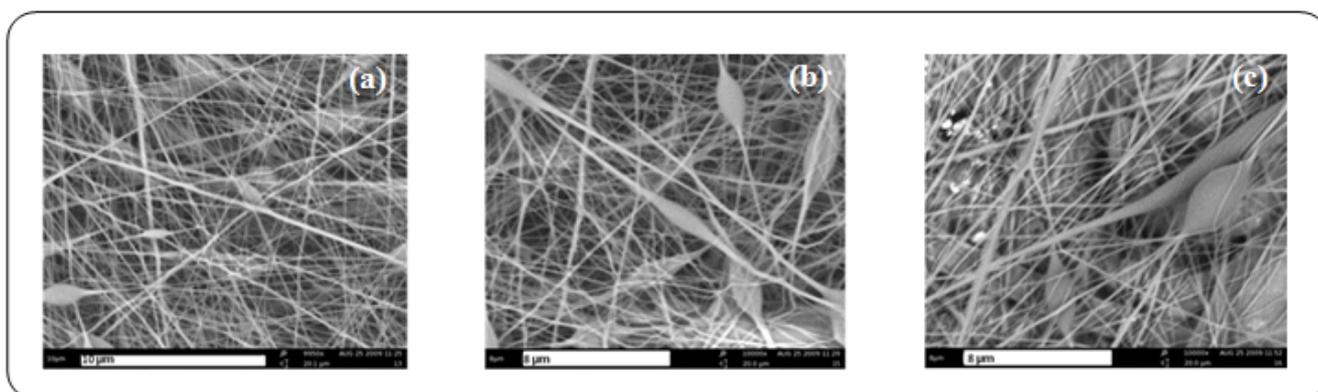


Fig. 8: SEM images of PVB fibres in different concentrations and molecular weights: (a) 6% wt PVB75+ n-butanol, (b) 7% wt PVB75+ n-butanol, (c) 10% wt PVB60+ n-butanol.

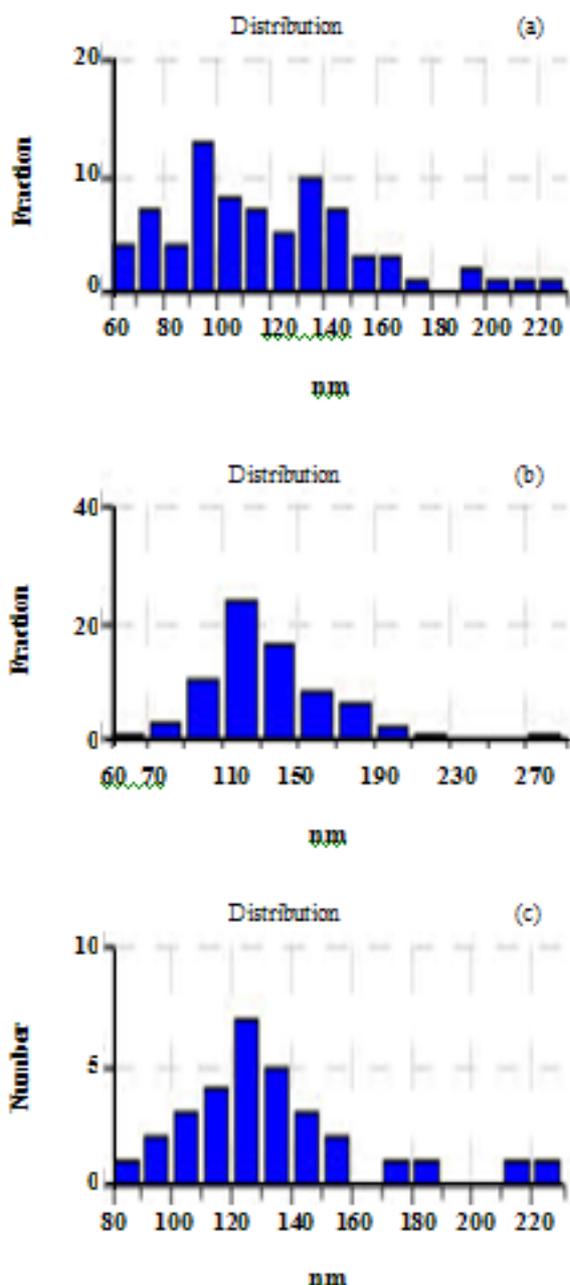


Fig. 9: Fibre diameter and distribution of PVB in butanol solution: (a) 6% wt PVB75+ n-butanol, (b) 7% wt PVB75+ n-butanol, (c) 10% wt PVB60+ n-butanol.

diameter, but not formation of beads. Table 2 compares the fibre uniformity coefficient (A_w/A_n) for all polymer solutions.

Table 2 reveals that the diameter coefficient for all fibres is around "1". Rather than having different average diameters, almost all fibre diameters are uniform. Average fibre diameters are shown in Table 3.

Changing the concentration of the polymer adversely affected the results concerning the quality of nanofibres produced. It is important to reduce the nanofibre diameter as much as possible, since the mechanical properties improve as fibre diameter is reduced. Reduction of nanofibre diameter was achieved by lowering the concentration and molecular weight of the PVB, but at low concentration bead formation was observed.

Due to having a lower molecular weight, PVB60 polymer solutions had a smaller diameter than PVB75H. As shown in Table 3 PVB+n-butanol polymer solutions have the smallest fibre diameter. However there was bead formation on the surface of the fibres. PVB+isopropanol solutions were easily spinnable and fibre diameters were quite low in comparison with PVB+ethanol. The solvent effect is comparable for each solution. Isopropanol is a good solvent for both PVB60H and PVB75H. On the other hand, ethanol is a good solvent for PVB60H.

CONCLUSIONS

In this study, the effect of using different kinds of solvent with the polymer PVB, and the effect of molecular weight and concentration on electrospinning, were investigated. Higher molecular weight and higher concentrations represent higher polymer chain entanglements. Lower concentrations and lower molecular weight represent lower fibre diameter; however, beads were observed in the butanol solvent.

By using isopropanol and butanol, fibre diameters were kept very low, but bead formation was observed. Both n-butanol and isopropanol have a high boiling point and low dipole moment. Dielectric constants are the same. It seems that fibre diameter can be controlled via solvents. PVB+n-butanol solutions yielded very thin fibres, but with beads. Isopropanol solvent had a good result for both PVB60H and PVB75H. Ethanol solvent is suitable only for PVB60H. Our results showed that nearly all solutions based on isopropanol, butanol and ethanol, were good solvents for PVB in the production of nanofibres. Fibre uniformity was nearly at an optimum level.

The results suggested that, without knowledge of viscosity, surface tension and solvent conductivity and the resulting solutions, productivity and morphological appearance (e.g. fibre diameter, bead formation) could be predicted by considering the solvent properties (Table 1) alone.

Table 2: Comparison of the fibre diameter coefficient of PVB polymer fibres.

Polymer Solution	6% Concentration	7% Concentration	10% Concentration
Ethanol+PVB60H	1,041404	1,060709	1,081017
Ethanol+PVB75H	1,029978	1,142213	1,40471
Isopropanol+PVB60H	1,026316	1,051471	1,090395
Isopropanol+PVB75H	1,022364	1,095823	-
n-Butanol+PVB60H	-	-	1,052632
n-Butanol+PVB75H	1,084034	1,067164	-

Table 3: Average fibre diameter of polymer solutions.

Polymer Solution	6% Concentration	7% Concentration	10% Concentration
Ethanol+PVB60H	128.69 ± 26.19 nm	191.81 ± 47.26 nm	410.78 ± 116.92 nm
Ethanol+PVB75H	580.07 ± 100.44 nm	712.8 ± 268.81 nm	1027.77 ± 116.92 nm
Isopropanol+PVB60H	152 ± 25.91 nm	136 ± 29.1 nm	354 ± 106.21 nm
Isopropanol+PVB75H	313 ± 46.59 nm	407 ± 126.58 nm	-
n-Butanol+PVB60H	-	-	133 ± 30.92 nm
n-Butanol+PVB75H	119 ± 34.87 nm	134 ± 34.7 nm	-

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